

# Itinerancy and Electron Correlation in FeSe<sub>1-x</sub> Superconductor Studied by Bulk-Sensitive Photoemission Spectroscopy

A. Yamasaki,<sup>1,2</sup> S. Imada,<sup>3</sup> K. Takase,<sup>4</sup> T. Muro,<sup>5</sup> Y. Kato,<sup>5</sup> H. Kobori,<sup>1,2</sup>  
A. Sugimura,<sup>1,2</sup> N. Umeyama,<sup>6,7</sup> H. Sato,<sup>8</sup> Y. Hara,<sup>9</sup> N. Miyakawa,<sup>6</sup> and S. I. Ikeda<sup>7</sup>

<sup>1</sup>*Faculty of Science and Engineering, Konan University, Kobe 658-8501, Japan*

<sup>2</sup>*Quantum Nanotechnology Laboratory, Konan University, Kobe 658-8501, Japan*

<sup>3</sup>*College of Science and Engineering, Ritsumeikan University, Kusatsu 525-8577, Japan*

<sup>4</sup>*College of Science and Technology, Nihon University, Chiyoda, Tokyo 101-8308, Japan*

<sup>5</sup>*Japan Synchrotron Research Institute, Sayo, Hyogo 679-5198, Japan*

<sup>6</sup>*Department of Applied Physics, Tokyo Institute of Technology, Shinjuku, Tokyo 162-8601, Japan*

<sup>7</sup>*Nanoelectronics Research Institute, AIST, Tsukuba 305-8568, Japan*

<sup>8</sup>*Faculty of Science and Engineering, Chuo University, Bunkyo, Tokyo 112-8551, Japan*

<sup>9</sup>*Ibaraki National College of Technology, Hitachinaka 312-8508, Japan*

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We have investigated the electronic structures of newly discovered superconductor FeSe<sub>1-x</sub> by bulk-sensitive photoemission spectroscopy (PES). The large Fe 3d spectral weight is located in the vicinity of the Fermi level ( $E_F$ ) and it decreases steeply toward  $E_F$ . Compared with results of band structure calculations, narrowing the Fe 3d band width and the energy shift of the band toward  $E_F$  are found, suggesting a mass enhancement due to the weak electron correlation effect. Meanwhile, Fe 2p core-level PES reveals a strong itinerant character of Fe 3d electrons. These features are very similar to those in other Fe-based high- $T_c$  superconductors.

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Fe-based high- $T_c$  superconductors have attracted enormous attention for their possibly new-type superconducting mechanism and the potential of breaking the deadlock in the high- $T_c$  superconductor research field. A fluorine doped LaFeAsO has been discovered to be a superconductor below  $T_c = 26$  K, which contains the two dimensional Fe plane in the Fe<sub>2</sub>As<sub>2</sub> layer [1]. So far, more than forty kinds of superconductors in several types of mother materials such as LaFeAsO, CaFeAsF, BaFe<sub>2</sub>As<sub>2</sub>, and LiFeAs, have been synthesized [2]. Among them, the highest  $T_c$  is recorded to be 56 K in Gd<sub>1-x</sub>Th<sub>x</sub>FeAsO [3]. Recently, only the Fe-included layer, namely, Fe<sub>2</sub>Se<sub>2</sub> layer has been revealed to show superconductivity [4]. The appearance of the superconductivity in the oxygen-free Fe compound FeSe<sub>1-x</sub> indicates Fe<sub>2</sub>X<sub>2</sub> ( $X = \text{P, As, and Se}$ ) layer is essential for the superconductivity in these Fe-based high- $T_c$  superconductors. The density functional study has pointed out that the FeSe<sub>1-x</sub> is not a conventional electron-phonon superconductor, being similar to LaFeAsO<sub>1-x</sub>F<sub>x</sub> system [5]. These newly discovered Fe-based superconductors have some commonalities, such as the two dimensional Fe plane, the Fe atom located in the tetrahedrally coordinated ligands, and the carrier doping as in high- $T_c$  cuprates.

The layered FeSe has the  $\alpha$ -PbO-type crystal structure. In the off-stoichiometric composition FeSe<sub>1-x</sub> ( $x \simeq 0.01$ -0.08) superconductivity appears, which is possibly induced by the electron doping to the two dimensional Fe plane [4, 6, 7, 8, 9]. FeSe has another stable crystal structure, namely, NiAs-type one which does not show superconductivity [7, 10]. The NiAs-type FeSe has an Fe atom surrounded by octahedrally coordinated Se atoms and the two dimensional Fe network. There are few ex-

perimental studies which have ever been done for the superconducting (SC) FeSe<sub>1-x</sub> although the NiAs-type FeSe<sub>x</sub> has been well studied for more than a half century [10, 11]. To obtain a deeper understanding of the superconductivity in FeSe<sub>1-x</sub>, an experimental study giving direct information on the electronic structures has been required.

In this Letter, we report on the detailed electronic structures of the SC FeSe<sub>1-x</sub> measured by soft-x-ray photoemission spectroscopy (SXPES). In addition, non-superconducting (NSC) FeSe<sub>x</sub> is investigated as a reference material. It is found in the SC FeSe<sub>1-x</sub> that the large Fe 3d spectral weight is located in the vicinity of  $E_F$  and it decreases steeply toward  $E_F$ , being similar feature to those in the other Fe-based superconductor LaFeAsO<sub>0.94</sub>F<sub>0.06</sub>. Narrowing the Fe 3d band width and the energy shift of the band toward  $E_F$  suggest a mass enhancement due to the electron correlation effect. Meanwhile, a strong itinerant character of Fe 3d electrons has been revealed in Fe 2p core-level PES. The itinerant nature of Fe 3d electrons with the weak electron correlation, which also have been revealed in LaFeAsO<sub>0.94</sub>F<sub>0.06</sub>, would be a key feature in the newly discovered Fe-based high- $T_c$  superconductors.

SXPES has been widely recognized as one of the powerful techniques which can reveal bulk electronic structures due to the long inelastic mean free path (or the long effective attenuation length) of photoelectrons excited by soft x ray [12, 13, 14, 15]. The SXPES was carried out at the Figure-8 undulator SX beamline BL27SU in SPring-8 using the SPECS PHOIBOS 150 hemispherical electron energy analyzer [16]. The highest total energy resolution  $\Delta E$  was set to 75 meV at  $h\nu = 600$  eV. For the measure-

ments, single-crystal-like SC  $\text{FeSe}_{1-x}$  and NSC  $\text{FeSe}_x$  were employed, which were grown using Fe and Se powders and powdered  $\text{FeSe}$  as source materials, respectively. The SC  $\text{FeSe}_{1-x}$  samples have the transition temperature  $T_c^{\text{zero}} \simeq 6$  K ( $T_c^{\text{onset}} \simeq 13$  K) under ambient pressure in measurements of the in-plane electrical resistivity [17], which are similar to reported values [4, 6, 7, 8]. This implies the present samples have the tetragonal crystal structure and the selenium defect of few or several percent. In fact, both the SC and NSC samples have been confirmed to contain the tetragonal and hexagonal crystals by XRD (x-ray diffraction) measurements. The coexistence of two stable phases has also been reported by other groups [8, 9]. Details of the sample growth and their characteristics will be reported elsewhere [18]. Clean surfaces were obtained by fracturing samples *in situ* in UHV ( $\sim 4 \times 10^{-8}$  Pa) at the measuring temperature ( $T=16$  K). The fractured surface of the SC  $\text{FeSe}_{1-x}$  did not have a well-defined mirror plane to perform the angle-resolved PES measurement even though it might have a cleavage face. This is possibly caused by the imperfection of the crystal. We note that Fe  $2p$  and Se  $3d$  core-level PES spectra in SC and NSC samples have no superimposed structure which is due to the photoemission from both the tetragonal and hexagonal crystals. This indicates that the fractured samples have a single-phase crystal *at least* in the PES measurement area.

Figure 1 (a) shows valence-band PES spectra of SC  $\text{FeSe}_{1-x}$  and NSC  $\text{FeSe}_x$ . Both in the SC  $\text{FeSe}_{1-x}$  and NSC  $\text{FeSe}_x$ , the spectra have a sharp peak in the vicinity of Fermi level ( $E_F$ ). In addition, there are some broad peaks and hump structures at higher binding energy ( $E_B$ ) part. These structures consist of Fe  $3d$  and Se  $4p$  states as discussed later. In Fig. 1 (b), the valence-band PES spectra of the SC  $\text{FeSe}_{1-x}$  measured at three different photon energies are shown. The solid line and open circles indicate the spectra obtained at  $h\nu=900$  eV and 600 eV, respectively, which are labeled as “off-resonance” for comparison with another spectrum. It is found that these have the similar spectral shape, suggesting the variation of the ratio of Fe  $3d$  and Se  $4p$  photoionization cross sections between these two photon energies is negligible. The spectra also have the same features to recently reported one of the SC  $\text{FeSe}$  with the tetragonal structure [19]. The dashed line shows the spectrum which was measured at the energy just below the threshold of Fe  $2p$ - $3d$  absorption edge, labeled as “Fe  $2p$  anti-resonance”. In this spectrum Fe  $3d$  states are strongly suppressed since the tuned photon energy corresponds to the energy providing the minimum transition probability in the Fano lineshape [20]. One can see that the spectral weight between  $E_F$  and  $E_B=3$  eV is remarkably reduced. This indicates Fe  $3d$  dominant states are located in this  $E_B$  range. Some spectral weights still remain, suggesting that there are Se  $4p$  states hybridized with the Fe  $3d$  states. Meanwhile, no significant reduction below  $E_B=3$  eV is seen, since these structures mainly originate from Se  $4p$  states. We note that one often employs

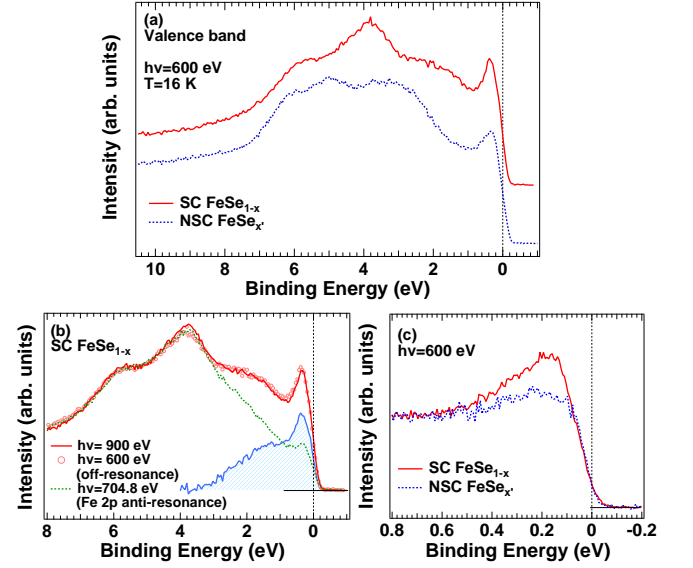


FIG. 1: (Color online) Valence-band PES spectra of SC  $\text{FeSe}_{1-x}$  and NSC  $\text{FeSe}_x$ . (a) Overall valence-band PES spectra measured at  $h\nu=600$  eV. These spectra are normalized by the area under the curves after subtracting the Shirley-type background. (b) Valence-band PES spectra of SC  $\text{FeSe}_{1-x}$  measured at three photon energies. The spectrum with the hatched area is difference between off-resonance (measured at  $h\nu=600$  eV) and anti-resonance spectra. (c) High-resolution PES spectra near  $E_F$ . Each spectrum is normalized so that the spectral intensity agrees with that in the lower-resolution spectrum in (a) at  $E_B=0.8$  eV.

the (on-) resonant PES to investigate the contribution of the specific electronic states by using the photon energy tuned to the core-level absorption maximum. In the present case, however, the Auger decay process becomes dominant and the valence-band structures are smeared out due to the large background.

The difference spectrum between the off-resonance ( $h\nu=600$  eV) and anti-resonance spectra is also shown in Fig. 1 (b), which represents the Fe  $3d$  partial density of states (PDOS). The overall valence-band and Fe  $3d$  spectral features qualitatively well correspond to the results of band structure calculations [5], in which the high Fe  $3d$  PDOS is located near  $E_F$  and the PDOS decreases steeply toward  $E_F$ . By analogy with the results of band structure calculations for  $\text{LaFeAsO}_{1-x}\text{F}_x$  [21, 22], all five Fe  $3d$  orbitals should have the finite weight between  $E_F$  and  $E_B=2$  eV due to the unclear crystal field splitting of the Fe  $3d$  states in the selenic tetrahedron. In the difference spectrum, narrowing the Fe  $3d$  band width and the energy shift of the band toward  $E_F$  are found, suggesting that the self-energy ( $\Sigma(\omega)$ ) correction is required to reproduce it by means of the band structure calculation. Interestingly, the difference spectrum has very similar shape to the experimentally obtained Fe  $3d$  PDOS of  $\text{LaFeAsO}_{0.94}\text{F}_{0.06}$  [23]. Considering the similarity of experimental and calculated Fe  $3d$  PDOSs of both  $\text{FeSe}_{1-x}$

and  $\text{LaFeAsO}_{0.94}\text{F}_{0.06}$ , we conclude that the electron correlation in  $\text{FeSe}_{1-x}$  is not strong (the mass enhancement factor  $z^{-1} \simeq 2$  as is comparable to  $z^{-1}=1.8$  in the latter compound), being qualitatively consistent with the results of the LDA+DMFT (the local density approximation combined with the dynamical mean-field theory) study [24, 25]. We note that the peak position of the difference spectrum ( $\sim 170$  meV) is further shifted towards  $E_F$  compared with that in  $\text{LaFeAsO}_{0.94}\text{F}_{0.06}$  ( $\sim 250$  meV). The  $z^{-1}$  depends on the real part of the self energy  $\Re\Sigma(\omega)$  as follows:  $z^{-1} \equiv 1 - \partial\Re\Sigma(\omega)/\partial\omega|_{\omega=0}$  [26]. Therefore, the peak shift might bring in the slightly larger  $z^{-1}$  because of the larger negative slope of  $\Re\Sigma(\omega)$  at  $E_F$ .

Now we focus on the similarity and difference of the electronic structures between the SC  $\text{FeSe}_{1-x}$  and NSC  $\text{FeSe}_{x'}$ . They have different Se  $4p$  electronic structures between  $E_B=3$  and 8 eV as shown in Fig. 1 (a). Furthermore, Fe  $3d$  states near  $E_F$  also have different features. High-resolution PES spectra near  $E_F$  are shown in Fig. 1 (c). We note that each spectrum is normalized by the intensity of the lower-resolution spectrum, that is, the integrated intensity of whole valence-band PES spectrum. Both spectra of the SC  $\text{FeSe}_{1-x}$  and NSC  $\text{FeSe}_{x'}$  have the same peak position at  $E_B \simeq 170$  meV. The SC  $\text{FeSe}_{1-x}$ , however, has a larger spectral weight at the peak position than the NSC  $\text{FeSe}_{x'}$ . Meanwhile, it is found that both spectra have a weak but finite intensity at  $E_F$ , suggesting these compounds have a metallic nature but a characteristic of the low-carrier density as is the case with the other Fe-based and cuprate superconductors [27].

The Fe  $2p$  core-level PES spectra of the SC  $\text{FeSe}_{1-x}$  and NSC  $\text{FeSe}_{x'}$  are shown in Fig. 2. It is found that the overall spectral width in the  $2p_{3/2}$  component of the SC  $\text{FeSe}_{1-x}$  is narrow and there is no charge-transfer satellite, as seen in  $\text{LaFeAsO}_{0.94}\text{F}_{0.06}$  and Fe metal [23], suggesting Fe  $3d$  electrons have an itinerant character. In addition, the SC  $\text{FeSe}_{1-x}$  has a very sharp peak at the lowest  $E_B$  part in the  $2p_{3/2}$  component, as shown in Fig. 2 (b). The significant intensity of this sharp peak, which appears when conduction electrons screen the core-hole potentials, indicates the strong itinerant character of the Fe  $3d$  electrons. Meanwhile, the NSC  $\text{FeSe}_{x'}$  has a wide spectral width in the  $2p_{3/2}$  component and very similar spectral shape to NiAs-type  $\text{Fe}_7\text{Se}_8$  [28]. In order to have further information on the difference of electronic structures, Se  $3d$  (including Fe  $3s$  and  $3p$ ) core-level PES spectra of the SC  $\text{FeSe}_{1-x}$  and NSC  $\text{FeSe}_{x'}$  were measured. The Se  $3d$  core-level PES spectra in both compounds have a simple doublet peak structure originating from Se  $3d_{5/2}$  and  $3d_{3/2}$  components. It is found that the Se  $3d$  core level of the SC  $\text{FeSe}_{1-x}$  is located at the  $E_B$  which is about 300 meV higher than that of the NSC  $\text{FeSe}_{x'}$ . This chemical shift is caused by the structural difference between these compounds, being consistent with what Se  $4p$  states have the different structure in the valence band of these compounds. Both the Fe  $3s$  core level of the SC  $\text{FeSe}_{1-x}$  and NSC  $\text{FeSe}_{x'}$  have an asymmetric structure. It is, however, not clear whether the origin of the

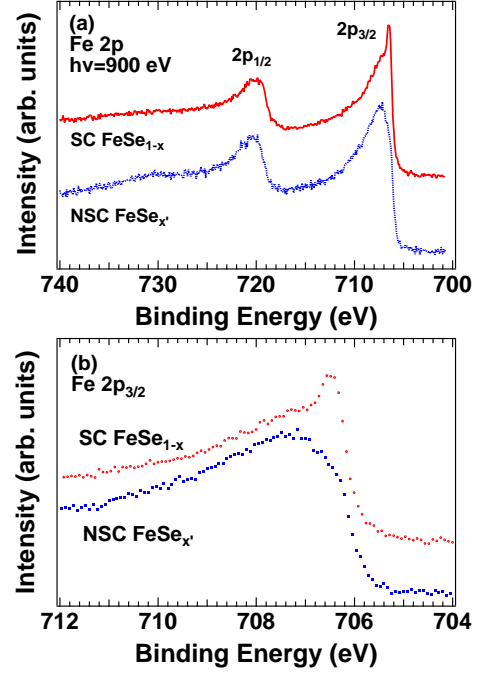


FIG. 2: (Color online) Fe  $2p$  core-level PES spectra of SC  $\text{FeSe}_{1-x}$  and NSC  $\text{FeSe}_{x'}$ . (a) Overall Fe  $2p$  core-level PES spectra. (b) The enlarged spectra in the Fe  $2p_{3/2}$  component.

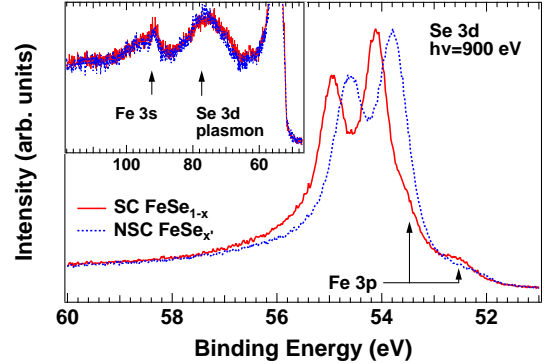


FIG. 3: (Color online) Se  $3d$  core-level PES spectra of SC  $\text{FeSe}_{1-x}$  and NSC  $\text{FeSe}_{x'}$ . The inset shows the spectra extended to higher  $E_B$ .

asymmetry is the exchange splitting or the 2<sup>nd</sup> plasmon satellite of Se  $3d$  core level.

In summary, we have performed the bulk-sensitive SX-PES for Fe-based superconductor  $\text{FeSe}_{1-x}$ . The band narrowing and the energy shift of Fe  $3d$  states suggest a mass enhancement due to the weak electron correlation effect, the strength of which might be similar to that in  $\text{LaFeAsO}_{1-x}\text{F}_x$  superconductor. Meanwhile, the SC  $\text{FeSe}_{1-x}$  has the strong itinerant Fe  $3d$  character unlike the NSC  $\text{FeSe}_{x'}$  as is revealed in the Fe  $2p$  core-level PES. The itinerant nature of Fe  $3d$  electrons with the weak electron correlation would be a key feature in the

newly discovered Fe-based superconductors.

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